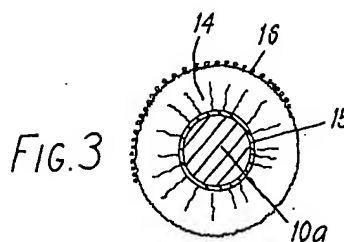


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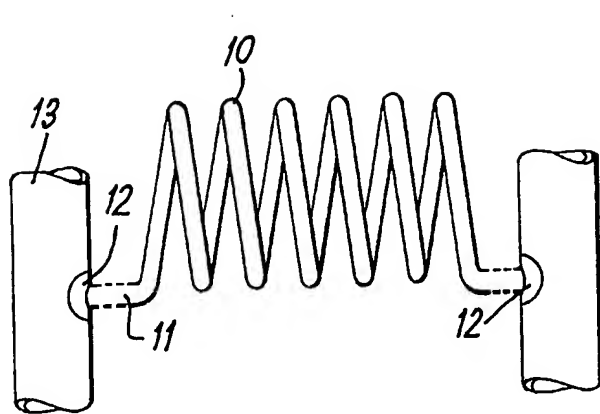
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(54) Catalytic gas sensor

(57) A catalytic gas sensing element comprises an inert metal base, such as a coil of platinum or platinum-containing wire 10a, a catalyst support comprising a coating 14 of titanium dioxide, and particles of catalytic metal 16, such as palladium or a palladium alloy, supported by the titanium oxide coating. The titanium oxide coating is preferably formed by deposition from the vapour phase by decomposition of titanium tetrachloride, either with the help of oxygen or of an aliphatic alcohol. Alternatively, the titanium oxide can be applied in suspension with an organic binder which is subsequently removed by heat.

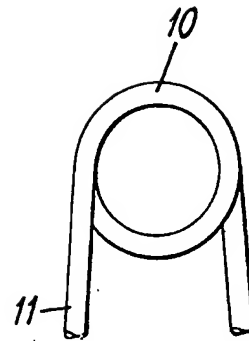


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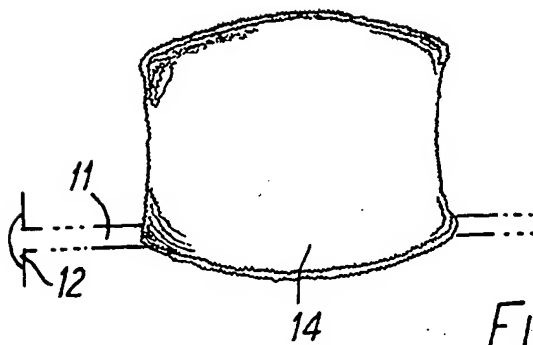


A

FIG. 1

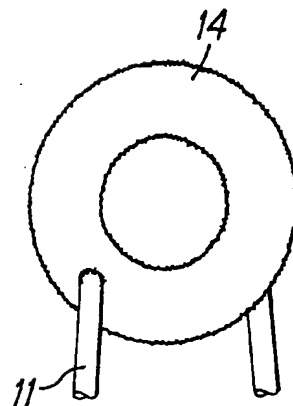


B



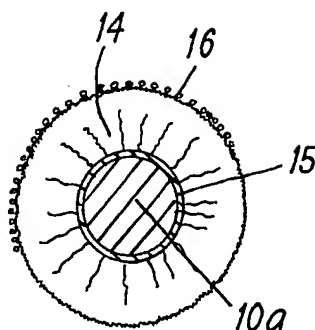
A

FIG. 2



B

FIG. 3



SPECIFICATION

Improved catalytic gas sensor

- 5 This invention relates to catalytic devices for use as gas sensors in apparatus for gas detection and analysis. 5
 The escape of gases such as hydrocarbons, carbon monoxide and hydrogen presents a considerable hazard in petrochemicals plants, coal mines and oil and gas production facilities. The only suitable method of detection presently available depends on the catalytic oxidation of any flammable gas present in the sampled atmosphere. The detecting element usually consists of a small metal coil, which acts both as a
 10 heater and a sensor, embedded in a bead of a refractory oxide such as alumina or thoria. This oxide is 10
 impregnated with a salt of a catalytically active metal. Combustion of the vapour of any hydrocarbon present causes a rise in temperature of the detecting element.
- In order to obtain a signal which is tolerably independent of temperature, such gas detection devices are usually operated under conditions where the rate of oxidation on the catalyst depends on the rate of
 15 diffusion of the reactive gas to the catalyst surface. Diffusion control is achieved by maintaining an ample 15
 amount of catalyst at a temperature high enough to ensure that the rates of adsorption, surface reaction and desorption, are relatively high.
- In practice, however, catalytic sensors lose activity after prolonged use at high temperatures or after operation in gas-rich atmospheres. This may be due to agglomeration of crystallites of the active component
 20 or to breakdown of the refractory oxide support caused by thermal shock. The latter mode of deactivation is 20
 helped by the fact that, using conventional methods of deposition of the refractory metal oxide which involve the thermal decomposition of a water-soluble precursor of that oxide, a poor bond is formed between the base metal and the oxide.
- The present invention is directed to the provision of a new and superior sensing element which displays
 25 catalytic gas detectors, desirable efficiency, mechanical strength and thermal shock resistance. A catalytic 25
 gas sensing element in accordance with this invention comprises an inert metal base, usually in the form of a wire coil, a catalyst support comprising titanium (IV) oxide (titania) coated on the metal base, and a catalytic metal supported by the said titania coating.
- For the purpose of the present invention, it is particularly preferred that the titania should be deposited on
 30 the metal base from the vapour phase by the decomposition of titanium (IV) chloride. The metal coil is 30
 preferably heated to a temperature in the range 500-1000°C.
- In a first variant of the vapour deposition process, titanium (IV) chloride vapour and oxygen are passed over the heated metal base. Pure oxygen can be used for this purpose, but it is preferred that the gas stream be diluted with an inert gas, for example helium or argon, because the increased flow rate then possibly
 35 creates greater turbulence around the metal to be coated. In a second variant, the vapours of titanium (IV) 35
 chloride and an aliphatic alcohol such as methanol are passed over the heated metal. The gas stream preferably includes an inert gas, for which purpose nitrogen is suitable, and optionally also ammonia. The titanium chloride and the alcohol are conveniently introduced in separate inert gas or ammonia streams and mixed in a reactor containing the heated metal.
- 40 An alternative method for the deposition of the titania catalyst support is the application to the metal base, 40
 preferable by electrodeposition, of a "paint" or suspension of pigment grade titania (anatase or rutile) in a liquid medium or vehicle containing an organic binder. The vehicle is removed by evaporation and the binder removed when the coil is heated. The titania may consist of substantially spherical particles having diameters in the range from 0.1 to 0.4 μ (100 to 400 nm).
- 45 The metal base or wire employed should be one to which the catalyst support will adhere, if necessary 45
 after a pre-treatment of the wire. It should also be corrosion-resistant and have suitable and predictable temperature/resistance characteristics. For enhanced long term stability it is preferred that the wire and the catalyst support should have similar thermal expansion properties. Especially suitable are platinum metals and alloys, such as platinum itself, a platinum-rhodium alloy, or a platinum palladium alloy, but the use of
 50 complex base metal alloys such as iron-chromium-aluminium-yttrium is also contemplated if they have 50
 suitable temperature coefficients of resistivity.
- A preferred form of metal base comprises a free-standing coil of platinum - containing wire of overall diameter 0.5-1.0 mm and overall length 0.5-1.0 m consisting of 6-10 turns of 0.025-0.050 mm wire, upon which is deposited the catalytic support.
- 55 The active metal dispersed of the support coating is preferably a noble metal of Group VIII of the 55
 Mendeleev Table of elements or a mixture or alloy of such metals, and may constitute, for example, from 0.5 to 25% of the weight of the catalyst. Especially preferred is platinum or palladium, or a platinum - palladium alloy, for example in the composition range 3:1 to 1:3, or a mixture of palladium with up to 10% of one of the metals copper, rhodium, erbium, osmium and cerium. It is preferred moreover that the (noble) metal
 60 particles should have diameters ranging from 1.0 to 50.0 nm, with the most frequently observed diameter 60
 between 1.0 and 2.5 nm.
- The catalytically active metal should be uniformly deposited on or distributed in the support coating and is preferably deposited in the form of a dilute aqueous solution of one or more of its compounds or of compounds of its components.
- 65 A preferred process for preparing a catalyst comprises impregnating titania with a compound of palladium 65

or a compound of platinum, or a mixture of compounds of platinum or palladium, or a mixture of compounds of either palladium or platinum and one of the metals copper, rhodium, erbium, osmium and cerium, drying the titania so impregnated and calcining this product by contact with helium gas or a methane - air (7% v/v CH₄) mixture at high temperatures (400 - 600°C).

- 5 The devices obtained by the process described may be used to catalyse the oxidation of gases such as carbon monoxide, hydrogen and many known hydrocarbons (particularly methane) which are encountered in industrial environments. Such oxidation reactions conventionally are carried out at temperatures in the range 200 to 600°C. The catalytic elements are of superior performance as gas detectors by virtue of the fact that they are mechanically extremely strong, behave repeatably towards a range of flammable gases and have enhanced stability in the presence of an atmosphere may be either rich in the flammable component or contain little of the same. 10

In the accompanying drawings Figure 1 A and B are respectively side and end views of the base structure of a catalytic gas sensor;

- 15 Figures 2 A and B are side and end views of the structure of Figure 1 coated with titania in accordance with the invention; and 15

Figure 3 is a cross section of a single turn of wire in a catalyst of this invention.

The structure shown in Figures 1 A and B is a wire coil 10, the ends 11 of which are extended and terminate in spot welds 12 on supports 13.

- 20 After being coated, the structure has the appearance shown in Figure 2, where the coil is covered by a coating of finely crystalline titania 14. 20

The titania-coated structure then receives a deposit of the catalytic metal, and the finished sensor when sectioned has the appearance shown in Figure 3. The wire 10a forms a core which is surrounded by a thin oxide coating 15 on the wire, the titania coating 14 and a surface coating of the catalyst particles 16.

- 25 The following examples illustrate the application of titania to base metal supports in the course of preparation of catalytic gas sensors according to the invention and the application of noble metals to titania supports. 25

Example 1

- 30 Titania was deposited on a coil of the metal base according to the following procedure. A coil of 0.025 mm platinum wire consisting of six turns of the same was mounted within a spherical reactor of 500 cm³ capacity. The reactor had provision for the mounting of several such coils and for the introduction and venting of a gas stream. Such a gas stream was composed of a mixture of carefully dried oxygen and helium which had been bubbled through a reservoir containing liquid titanium (IV) chloride. 30

- 35 The platinum coil was electrically heated to mean temperatures within the range 500 to 1000°C by the passage of a current from a constant resistance circuit. Thus, a pre-mixed flow of helium and oxygen (oxygen flow 100 mls min⁻¹; helium flow 0 - 100 mls min⁻¹) was bubbled through a reservoir of titanium (IV) chloride, the temperature of which was thermostatically controlled. This gas stream was thence led into the reactor. After a period of time, between one and eight hours, but usually two hours, a suitable bead of titania had formed around the coil. The titania so produced was in its rutile modification and consisted of fine crystallites, 1 to 4μ in diameter. 35

- 40 In a similar example, argon was substituted for helium. 40

- Upon such a titania bead, a catalytic metal was deposited according to the following method. A solution of palladium (II) chloride in very dilute hydrochloric acid or tetrammine palladium (II) chloride in water was prepared having a palladium content such that the application of 1 microlitre of the solution to the bead deposited material resulted in a metal loading of 2 to 15 percent by weight. After a conditioning process in which the impregnated bead was heated and exposed to a mixture of air and methane, its suitability as a gas sensor was ascertained by placing the device in an atmosphere containing 50% of the lower explosive limit (LEL) of gases such as methane, hydrogen, butane or carbon monoxide and measuring the electrical output of the device (in volts) as the applied current is increased (the initiation current) is an approximate measure of the catalytic activity of the bead whilst the output voltage reflects the sensitivity of the device to the gas. 45

- 50 Example 2 50

- 55 Titania was deposited on a coil of the metal base according to the following procedure. The coil was mounted in a spherical reactor according to Example 1. Into the reactor was introduced separately a stream of nitrogen containing titanium tetrachloride vapour and a stream of either nitrogen or ammonia or nitrogen containing ammonia also containing the vapour of an aliphatic alcohol such as methanol. Vapours of the alcohol and the titanium compound were introduced into the gas streams by bubbling the gas through thermostatted reservoirs containing these compounds. For example, a nitrogen stream containing titanium (IV) chloride vapour (100 ml min⁻¹) was introduced to the reactor together with a stream of ammonia gas containing methanol vapour (100 ml min⁻¹). On raising the temperature of the coil to 590 ± 40°C, a suitable bead of titania (in its rutile modification) was deposited on the metal base after fifteen minutes. 55

- 60 In a further example, a stream of nitrogen containing titanium tetrachloride (100 ml min⁻¹) was introduced to the reactor together with a stream of ammonia in nitrogen (1% volume/volume ammonia) (100 ml min⁻¹) which also contained methanol. On raising the temperature of the coil to 795 ± 15°C, a bead was produced after 20 minutes running. This bead, as formed, was black in colour but subsequent heating in air produced a typically white bead or rutile. 60

- 65 The titania beads produced by these methods were impregnated with the salt of a precious metal as 65

indicated in Example 1.

Example 3

Titania was supported on a base metal coil (19½ turns of 0.037 mm platinum wire) which itself was supported on woven silica, available as Refrasil, according to the following procedure. A paint consisting of a conventional water-based emulsion system with a dispersed organic polymer and containing titanium dioxide in the form of pigment grade anatase or rutile was placed in a stainless steel container. This container was connected to the anode of a variable voltage supply, the metal coil being connected to the cathode. On the passage of current, a deposit of paint was produced on the metal coil. Deposition voltages required were within the range 60 - 170 v and deposition times were in the range 60 - 240 seconds. After washing the coil with distilled water to remove excess titania, the organic charge-carrying resins were decomposed by passing a current through the paint-coated wires. Thereafter, the residual titania was impregnated with a precious metal salt as indicated in Example 1.

When titania sensors made in Examples 1 and 2 were exposed to 50% LEL of a number of gases and their responses measured, they compared favourably with sensors made from alumina and thoria. Thus, in Table 1, are shown the initiation currents and the bridge outputs, for a range of gases at a concentration of 50% LEL in air, when current-voltage curves were measured for pairs of sensors with the bridge balanced at 180 mA for each pair.

Table 1 Comparison of Response of Titania Gas Sensors with the Response of Similar-Sized, Conventional Devices

(a): means results for Pd/A₁O₃-ThO₂ sensors.
(b) and (c): results for Pd/TiO₂ sensors.

Gas	Initiation Current (mA)			Bridge Output (mV)		
	(a)	(b)	(c)	(a)	(b)	(c)
CO	99.3	117.0	111.0	37.2	44.0	42.0
H ₂	88.4	47.0	39.0	27.1	32.0	34.0
nC ₄ H ₁₀	154.2	145.0	135.0	22.0	27.0	26.0
CH ₄	161.0	148.0	140.0	34.8	18.0	20.0

In Table 2(a) and (b), results are given which show the results of gas tests on TiO₂-based devices made according to Example 3 when compared with similarly constructed sensors based on A₁O₃ and ThO₂.

Table 2 (a) Sensitivities (mV at 200 mA) to a Range of Gases

Gas	Typical A ₁ O ₃ -ThO ₂ device (mean of 8)	TiO ₂ (1)	TiO ₂ (2)	TiO ₂ (3)
CH ₄	450	450	550	500
n-C ₄ H ₁₄	343	325	400	330
CO	620	750	650	900
H ₂	442	400	300	-

Table 2 (b) Current (mA) at which Sensor Responds to 50% LEL Gas

Gas	Typical A ₁ O ₃ -ThO ₂ device (mean of 8)	TiO ₂ (1)	TiO ₂ (2)	TiO ₂ (3)
CH ₄	171	178	164	170
n-C ₄ -H ₁₀	164	176	155	160
CO	124	123	123	125
H ₂	91	53	46	-

Although the Tables disclose some inevitable variations in results, it is clear from Table 2 (a) that the TiO₂ devices are at least equal to and usually substantially better than ThO₂ with respect to CH₄ and CO.

In Table 2 (b), the more sensitive the device, the lower the current at which the sensor responds to gas. In eight out of eleven cases the TiO₂ sensors are more sensitive than the corresponding devices with ThO₂.

5 Sensors made according to Example 1 also compare favourably with ThO₂-Al₂O₃ supported devices. This is shown by the following Table 3 in which the initiation current and bridge output of the TiO₂ devices of Example 1 are compared with commercially available pellistors. It will be seen that the TiO₂ devices are substantially more sensitive (lower initiation current) than the ThO₂-Al₂O₃ devices to all the gases except CO.

10

Table 3 Comparison of Response of Titania Gas Sensor with the Response of Pd/Al₂O₃ - ThO₂ Pellistors

15	Gas	Pe	Initiation Current (mA)						Pe*	Bridge Output (mV)						15
			(a)	(b)	(c)	(d)	(e)	(f)		(a)	(b)	(c)	(d)	(e)	(f)	
	CH ₄	150-160	134	148	140	150	183	167	35-55	190	180	200	120	200	300	
	n-C ₄ H ₁₀	147-154	128	145	135	135	158	159	22-31	300	220	260	180	210	290	20
20	CO	100-108	-	117	111	112	-	132	37-59	-	440	420	280	-	400	
	H ₂	70-90	-	47	39	46	79	82	21-27	-	320	340	280	400	420	

25 Pe Refers to the results for several commercially obtainable Pd/Al₂O₃ - ThO₂ pellistors.

Pe* Response obtained under conditions wherein access of the gas to the device was restricted.

(a) - (f) Refers to similar devices based on TiO₂ without built-in restrictor.

30

CLAIMS

1. A catalytic gas sensing element comprising an inert metal base, a catalyst support comprising titanium (IV) oxide coated on the metal base, and a catalytic metal supported by the titanium oxide coating.

35 2. A gas sensing element according to claim 1 in which the inert metal base is a coil of platinum-containing wire.

3. A gas sensing element according to claim 2 in which the inert metal base is a free-standing coil of overall diameter 0.5 - 1.0 mm and overall length 0.5 - 1.0 mm consisting of turns of wire of 0.025 - 0.050 mm diameter.

40 4. A gas sensing element according to any of claims 1 to 3 in which the titanium oxide is vapour-phase deposited.

5. A gas sensing element according to any of claims 1 to 3 in which the titanium dioxide is in the form of substantially spherical particles with diameters in the range 100 to 400 nm.

45 6. A gas sensing element according to any of claims 1 to 5 in which the catalytic metal comprises one or more of the noble metals of Group VIII of the Mendeleev Table and constitutes from 0.5 to 25% of the weight of the catalytic element.

7. A gas sensing element according to any of claims 1 to 6 in which the catalytic metal is palladium, or a palladium-platinum alloy in the proportions of 3:1 to 1:3 or a mixture of palladium with up to 10% of copper, rhodium, erbium, osmium or cerium.

50 8. A gas sensing element according to claim 6 or 7 in which the catalytic metal has a particle size in the range 1.0 to 50 nm.

9. A method of making a catalytic gas sensing element by coating an inert metal base with a catalyst support layer comprising titanium (IV) oxide and thereafter depositing a catalytic metal thereon, wherein the titanium oxide coating is deposited from the vapour phase by decomposition of titanium (IV) chloride.

55 10. A method according to claim 9 in which the titanium chloride vapour and oxygen are brought into contact with the heated metal base.

11. A method according to claim 9 in which the vapours of titanium chloride and an aliphatic alcohol are brought into contact with heated metal base.

12. A method according to claim 10 or 11 in which the vapours are diluted with an inert gas.

60 13. A method according to any of claims 10 to 12 in which the metal base is heated to 500-1000°C.

14. A method of making a catalytic gas sensor by coating an inert metal base with catalyst support layer comprising titanium (IV) oxide and thereafter depositing a catalytic metal thereon, wherein the titanium oxide layer is formed by applying to the base a suspension of pigment grade anatase or rutile in a liquid medium containing an organic binder, removing the liquid by evaporation and heating the coil to remove the binder.

65

15. A method according to claim 14 in which the base is immersed in the suspension and the oxide deposited thereon by electro-deposition.
16. A method of making a catalytic gas sensor substantially as described in any of the Examples herein.
17. A catalytic gas sensor made by a method according to any of claims 9 to 16.

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